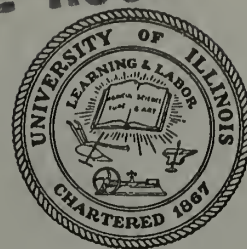


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EFFECT OF PHOSPHATES ON WATER TREATMENT

Phase II. Studies on the Degradation of Condensed Phosphates

By

R. S. ENGELBRECHT

LU BELLE BOICE

and

JAMES J. MORGAN

FINAL REPORT FOR THE PERIOD
JUNE 15, 1955 TO SEPTEMBER 15, 1957

for the

ASSOCIATION OF AMERICAN
SOAP AND GLYCERINE PRODUCERS

UNIVERSITY OF ILLINOIS
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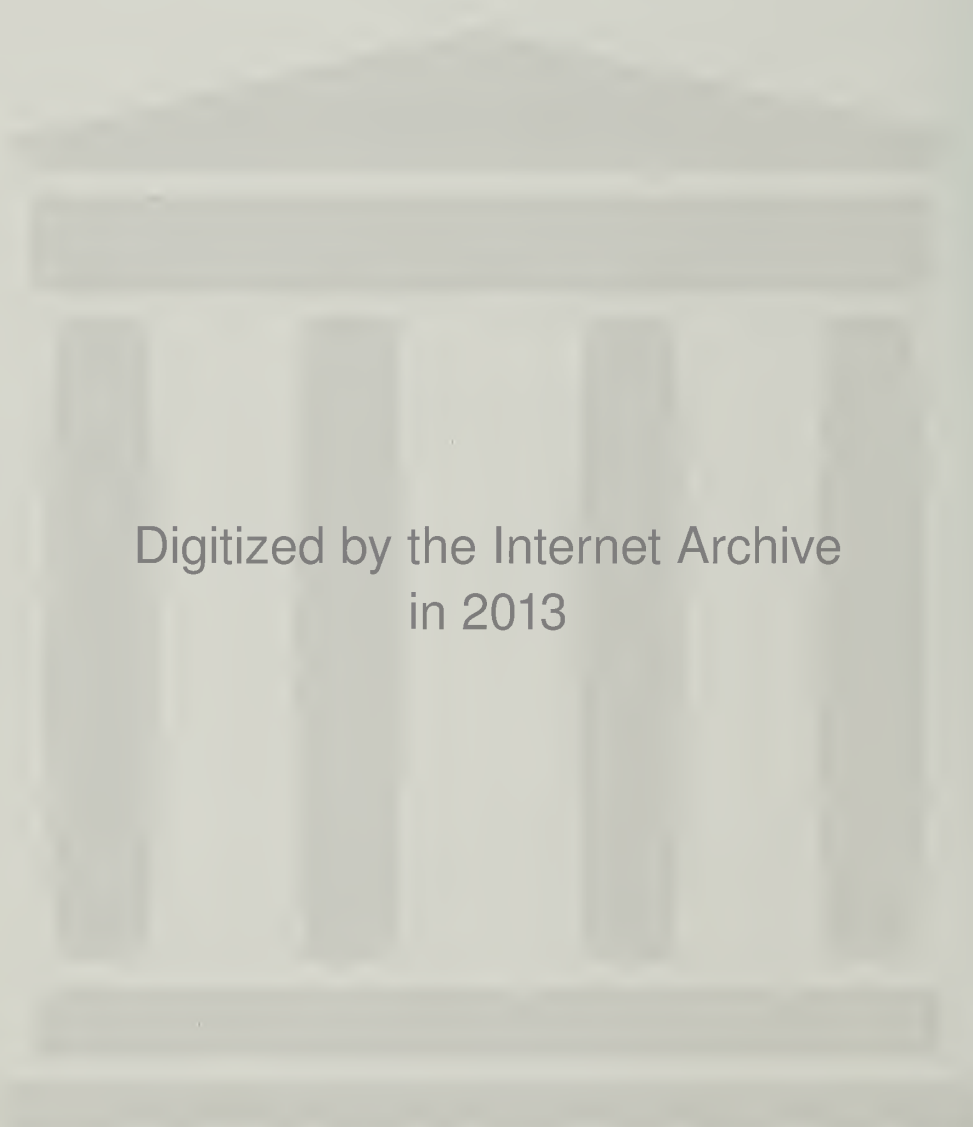
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Sanitary Engineering Laboratory
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July 1958



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ABSTRACT

The degradation of the condensed phosphates, sodium tripolyphosphate (STP) and tetrasodium pyrophosphate (TSPP), was studied in natural waters by adding these compounds to various lake, reservoir, and stream samples. Following pretreatment of the samples, they were stored at constant temperature under quiescent, semi-quiescent, or turbulent conditions.

It was found that condensed phosphates, as represented by STP and TSPP, were subject to hydrolytic degradation in natural waters. Various rates of degradation were noted in different natural waters, having different chemical and physical characteristics. With the possible exception of the concentration of organic matter and hydrolyzable phosphate in the natural water, both of which appeared to increase the rate of degradation, there seemed to be no correlation between degradation rate and the chemical and physical characteristics of the waters. Different rates of degradation were also observed in the natural water samples which were collected at the same time but at different locations along a single river. Similarly, the rate of degradation varied in natural waters, collected at different times but at the same location.

Filtration of the raw water, in order to reduce suspended solids, including biological life, definitely decreased the rate of degradation. This result, along with bacteriological data and additional observations, indicated that biological life exerted an effect on the rate of degradation.

Of the condensed phosphates studied, STP degraded more rapidly than TSPP when the same natural water was used for storage. However, if the degradation of STP and TSPP was studied separately, using either different natural waters or different samples of the same water, TSPP could be observed to degrade faster than STP.

Using distilled water, it was found that the rate of degradation increased with temperature, but appeared to decrease as the concentration of condensed phosphate was increased.

ACKNOWLEDGEMENT

This report covers an investigation conducted in the Engineering Experiment Station of the University of Illinois, Department of Civil Engineering, and sponsored by the Association of American Soap and Glycerine Producers, from June 15, 1955 through September 15, 1957. The final report is being presented in three parts, corresponding to three phases of work. The first report Phase I, Phosphates in Illinois Surface Waters, was published in March, 1958 as Sanitary Engineering Series No. 5. The present report covers Phase II, Studies on the Degradation of Condensed Phosphates.

At various times during the period of investigation, the following were associated with this study: Dr. Jess C. Dietz, formerly Professor of Sanitary Engineering and initially Director of the project; Mr. Robert H. Harmeson, Research Associate and Instructor in Civil Engineering; and Mr. John R. Towers, Research Assistant. Their participation in the planning and execution of this project is gratefully acknowledged.

I. INTRODUCTION

There exists in the literature considerable information regarding the structure and properties of the various condensed phosphates or polyphosphates. Of interest in this study was the property of such compounds to undergo what is usually referred to as hydrolysis, hydration, reversion, or hydrolytic degradation. That is, these compounds have the tendency to react with water to form, ultimately, orthophosphate. This property, as well as others, have been discussed in several articles (1) (2) (3). In summary, it has been found that the rate of hydrolytic degradation of condensed phosphates is influenced by many factors, including: temperature; pH; enzymes; colloidal gels, e.g. hydrated oxides of iron and aluminum; complexing cations, e.g. calcium; concentration; and the ionic environment of the solution.

Because the "builders" or supplementary compounds in commercial synthetic detergents are largely condensed phosphates, these compounds are of particular interest as they appear and exist in sewage effluents and receiving waters. Therefore, the Phase I report of this investigation was concerned with the kind and concentrations of phosphates found in various Illinois surface waters (4). The objective of the second phase of study was to determine whether condensed phosphates persisted in natural waters or whether they underwent hydrolytic degradation to form simple orthophosphate. It is with Phase II that this report is concerned.

In relation to the objective of Phase II, there are several publications of particular interest. First of all, it should be pointed out that many of the investigations on hydrolytic degradation of condensed phosphates have been made using solutions with a concentration of 1 per cent or greater. Using sodium tripolyphosphate (STP), Bell (5) found that stability decreased slightly when the concentration of the compounds was increased from 1 per cent to 10 per cent.

This was of interest in view of the fact that in this study the greatest concentration of condensed phosphate used was 9.16 ppm as P_2O_5 or 0.000916 per cent.

Green (6) reported that calcium usually increased the rate of degradation. In his studies, he used solutions of sodium tripolyphosphate (STP) and tetrasodium pyrophosphate (TSPP) ranging in concentrations from 5 to 50 ppm phosphates or 3.7 to 37 ppm as P_2O_5 . Calcium was added in a concentration of 255 ppm as $CaCO_3$. Using a pH range of 5 to 9, he found that calcium increased the rate of degradation as the pH was increased; while in the absence of calcium, the rate decreased with higher pH values. Green also observed that with magnesium the rate of degradation was usually unaltered or decreased.

In studying the degradation of STP and TSPP in sewage, Sawyer found that STP was hydrolyzed much more slowly than TSPP (7). He also observed a greater rate of degradation of both compounds at $20^{\circ}C$ as compared to $5^{\circ}C$. Although it was not indicated, the half life of TSPP in sewage at $20^{\circ}C$ appeared to be in the order of 15 hours. It might be noted that sufficient STP and TSPP was added to the sewage to give an initial concentration of 10 ppm of phosphorus or 22.9 ppm as P_2O_5 .

The hydrolytic degradation of STP and TSPP was studied by Smith, Cohen and Walton (8), using natural waters. Ohio River water, which had a total hardness of 64 ppm, calcium hardness of 44 ppm, and an alkalinity of 23 ppm, all expressed as ppm $CaCO_3$; and to which STP was added equivalent to 20 ppm of phosphate, gave half life values of 240, 60, and 20 days at storage temperatures of 5° , 20° , and $35^{\circ}C$, respectively. The same source of water was used for a similar experiment using TSPP. Because this sample of Ohio River water was apparently collected at a different time, its chemical characteristics were different. This water

had a total hardness of 121 ppm, calcium hardness of 84 ppm and an alkalinity of 36 ppm, all expressed as ppm CaCO_3 . Using an initial TSPP concentration equivalent to 20 ppm of phosphate, the half life at 5° , 20° and 30° C was observed to be 220, 120 and 45 days, respectively. In addition to the chemical differences in these two Ohio River water samples, the sample used in the STP experiment had a turbidity of 248 ppm while that in TSPP study was only 77 ppm. Although the Ohio River water used in these two experiments differed in chemical and physical characteristics, it is of interest to note that in general STP had a greater rate of degradation than TSPP. This was in contrast to the findings of Sawyer (7) who used sewage rather than natural water. A third experiment was carried out by Smith and his co-workers using TSPP, but with a "Local Stream Water" which had a total hardness of 223 ppm, of which 162 ppm was calcium, expressed as ppm CaCO_3 . With this harder water, the half life at 5° , 20° , and 35° C was found to be 310, 180 and 75 days, respectively.

Using various species of the plant kingdom, Karl-Kroupa, et al. (3) studied the hydrolysis of STP under aseptic conditions. The medium used in this study was sterile distilled water to which STP was added in an amount equivalent to 5.5 ppm phosphorus or 12.6 ppm as P_2O_5 . The organisms studied were pretreated before inoculation into the test solution, so as to be pure cultures. With the exception of Escherichia coli, all of the organisms were in a resting condition. All of the systems showed a lag period or induction time before active degradation of the STP occurred. The half life of STP in the various systems containing different organisms varied from 19 hours for Allomyces to 123 hours for Elodea. The control, which consisted of sterile distilled water plus STP, showed no change in 300 hours (12.5 days). According to the authors,

these results indicated that the accelerated rate of hydrolytic degradation of STP in the systems containing the test plants was due to an enzymatic catalysis.

Regarding enzymatic activity, there exists a number of phosphatase enzymes capable of transforming condensed phosphates into orthophosphate (9). These enzymes, including the pyrophosphatases and metaphosphatases, have been demonstrated in extracts from various microorganisms, e.g., yeasts and mold. One study related showed that a water extract from Aspergillus niger converted a solution of either sodium metaphosphate or pyrophosphate quantitatively to orthophosphate during an incubation period of 2 hours at 30° C. In another study, it was found that STP was transformed into orthophosphate by enzyme extracts from microorganisms and organs of animals.

III. EXPERIMENTAL METHODS

General Procedure for Determining Degradation of Condensed Phosphates

The degradation studies were conducted in this manner:

1. The water sample, in which the rate of hydrolysis of condensed phosphate was to be measured, was collected, iced, and transported to the laboratory as rapidly as possible.
2. Following the analysis of the water sample for its physical and chemical composition, the sample was pretreated in accordance with the particular conditions of the experiment and brought to temperature equilibrium. Condensed phosphate was then added to the sample.
3. The water sample was stored at a constant temperature of 85°F., unless otherwise indicated, under conditions of quiescence, semi-quiescence, or constant agitation.
4. Degradation of condensed phosphate was followed by frequent analysis of the orthophosphate and hydrolyzable phosphate content in the sample.

Sampling

With regard to the source of the natural waters studied in this phase of the investigation, the Mattoon, Bloomington, Springfield, Kincaid, and Danville samples were collected from either lakes or reservoirs while the remainder were from streams. The locations of the various sampling stations were indicated in the Phase I report of this investigation (4). At the time of collection, each sample was analyzed for dissolved oxygen and the temperature of the water recorded. A larger sample was placed in a Pyrex carboy and immediately transported to the laboratory.

Treatment of Samples

1. Upon arrival at the laboratory, each water sample was analyzed for ortho and ortho-plus-hydrolyzable phosphate, alkalinity, total and calcium hardness, pH, and turbidity.
2. Filtration.

The early objective of this phase of work was to study the effect of plankton, soil particles and colloidal material on the hydrolysis of condensed phosphates using natural waters. Each water, returned to the laboratory for storage, was divided into two parts before addition of condensed phosphate; one part of the sample was filtered, while the other half was untreated.

In pretreating some waters, filtration was accomplished by using membrane filters under aseptic conditions, while in other cases, the plankton count and visible turbidity were reduced by final filtration through either fine filter paper (Whatman No. 1) or non-sterile membrane filters. While it was intended that aseptic membrane filtration would produce a sterile filtrate for storage, it was found that contamination occurred during either the pretreatment processing or the subsequent opening of the storage bottles for the purpose of sampling. Autoclaving was also employed as a method for sterilizing the natural water samples. Although data will be presented using this method of pretreatment, it was found that it altered the chemical composition of the water. After filtration, both portions of the sample (filtered and non-filtered) were divided into three portions; one portion each for quiescent, semi-quiescent and turbulent storage. The six portions were placed in sterile 4-liter serum bottles and brought to 85°F.

In other degradation studies, filtration of the samples was discontinued. Samples were placed directly into 4-liter serum bottles and brought to temperature equilibrium.

3. Additions of condensed phosphate.

In this study, the condensed phosphates used included: tetrasodium pyrophosphate (TSPP), Allied Chemical and Dye Corporation, reagent grade; and sodium tripolyphosphate (STP). The STP (hexahydrate) was purified from a commercial grade of STP by recrystallization, using the method of Quimby (10).

Sterile solutions of STP and TSPP were prepared by aseptic membrane filtration. Following pretreatment of the water samples, a calculated amount of this standard STP or TSPP solution was added to each aliquot or sample of water to be stored. The concentration of condensed phosphate in each sample was immediately determined.

The amount of condensed phosphate added to the water samples was determined by the upper level of condensed phosphate found in the general survey of Illinois surface waters reported under Phase I (4).

Conditions of Storage

During the time of condensed phosphate hydrolysis (storage), the samples were stored in a constant-temperature room maintained at $85 \pm 3^{\circ}\text{F}$. Quiescent samples were stored on a shelf. Semi-quiescent samples were stored on a revolving rack which was agitated by hand twenty-five times twice daily. Turbulent samples were stored on a continuously agitated, mechanical shaker.

Analytical Methods

Phosphate Determination: The method used throughout this study was based on the colorimetric determination of orthophosphate in a water sample before and after acid hydrolysis. The particular procedure employed in the first series

of runs: Mattoon, Bloomington, Kincaid, Springfield, Danville, and distilled water; involved an extraction and hydrolysis procedure and was transmitted to the laboratory by the Research Department, Inorganic Chemicals Division, Monsanto Chemical Company, Dayton, Ohio. A modification in the procedure, based on the results of a collaborative sample survey conducted by the Association of American Soap and Glycerine Producers, was used in the remainder of the storage runs.

In both procedures, phospho-molybdate was extracted with a benzene-isobutyl alcohol mixture and reduced with stannous chloride to give a blue color which was measured spectrophotometrically. Orthophosphate was obtained by making a colorimetric determination directly on the sample. The ortho-plus-hydrolyzable phosphate concentration was determined by first boiling the sample in an aqueous acid solution. The hydrolyzable phosphate, which was interpreted as apparent condensed inorganic phosphate, was then calculated by subtracting the ortho-phosphate previously determined. All results have been expressed in terms of P_2O_5 .

It was originally thought that the difference between ortho-plus-hydrolyzable phosphate and orthophosphate, as determined by the above procedure, yielded the concentration of condensed inorganic phosphate. It is now known that this is not the case. In 1957, the third collaborative study conducted by the Association of American Soap and Glycerine Producers Technical Advisory Subcommittee on Phosphates established that the acid hydrolysis step could cause hydrolysis of certain organic phosphates. Consequently, that which was being assumed to be condensed inorganic phosphate could consist in part of organic phosphate. Therefore, the results obtained by subtraction of orthophosphate from ortho-plus-hydrolyzable phosphate should be interpreted as being equal-to, or greater-than the true concentration of condensed inorganic phosphate. The

rate of hydrolysis or degradation of condensed phosphate during storage, determined from results obtained by this analytical method, could be influenced by the amount of organic phosphate present or produced in the sample.

Other Determinations: The determinations for hardness, alkalinity, turbidity, dissolved oxygen, and pH were performed in accordance with the analytical methods previously described (4). The Dichromate Reflux Method with silver sulfate catalyst was used for the determination of Chemical Oxygen Demand (C.O.D.). In general, all of the analytical determinations were made in accordance with the procedures set forth in the 10th Edition of Standard Methods for the Examination of Water, Sewage and Industrial Wastes (11).

Expression of Results

For simplicity, all of the results on degradation of condensed phosphate have been expressed in terms of "half life". This denotes the time required for 50 per cent of the condensed phosphate to be hydrolyzed to orthophosphate. The half life, in each storage study, was determined by plotting the per cent remaining against storage time.

IIII. EXPERIMENTAL RESULTS

In order to determine the reproducibility of the analytical procedure for phosphate and the other experimental techniques, six (6) replicate portions of a Ficklin A water sample were prepared for storage. After temperature equilibrium had been established, 3.0 ppm (P_{205}) of STP was added to each portion before storage under turbulent conditions. The mean half life was found to be 29 days. These data are shown also in Figure 1. Because of the ortho and hydrolyzable phosphate present in the original sample before the addition of STP, the curve does not intersect 100 per cent. The standard deviation was calculated to be 21 per cent.

A similar storage study was made using TSPP. An analysis of the results, as shown in Figure 2, gave a mean half life of 14 days. The standard deviation was found to be 8 per cent. Although both this study and that made with STP (Figure 1) utilized water collected at the Ficklin A sampling station, the two studies cannot be directly compared because the waters were obtained at different times.

Table 1 gives the chemical and physical characteristics of the natural waters used in the various storage studies, along with the source and date of collection. Since the amount of total hardness varied from 170 to 1050 ppm as $CaCO_3$, all of the waters can be considered to be relatively or very hard, with a considerable amount of calcium hardness. Except for the Mattoon, Kincaid, Springfield, Bondville (11/12/56) and Shelbyville (12/3/56) samples, all of the waters were found to contain some condensed or hydrolyzable phosphate.

The results for the general surface water storage studies, expressed as half life values, are presented in Table 2. Included in this table also is the

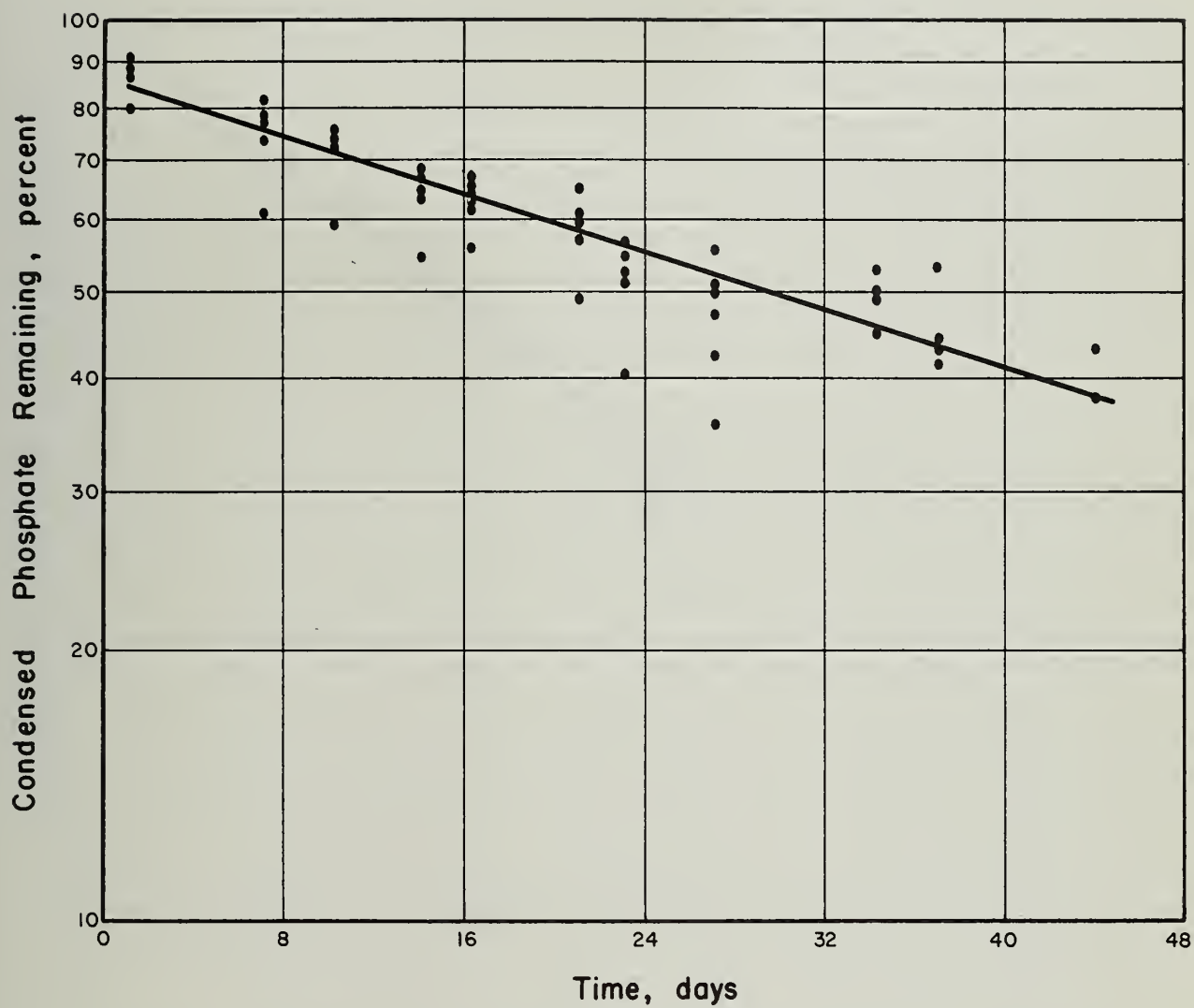


FIGURE 1. Degradation of 3.0 ppm (P_2O_5) STP in six portions of the same Ficklin A water sample.

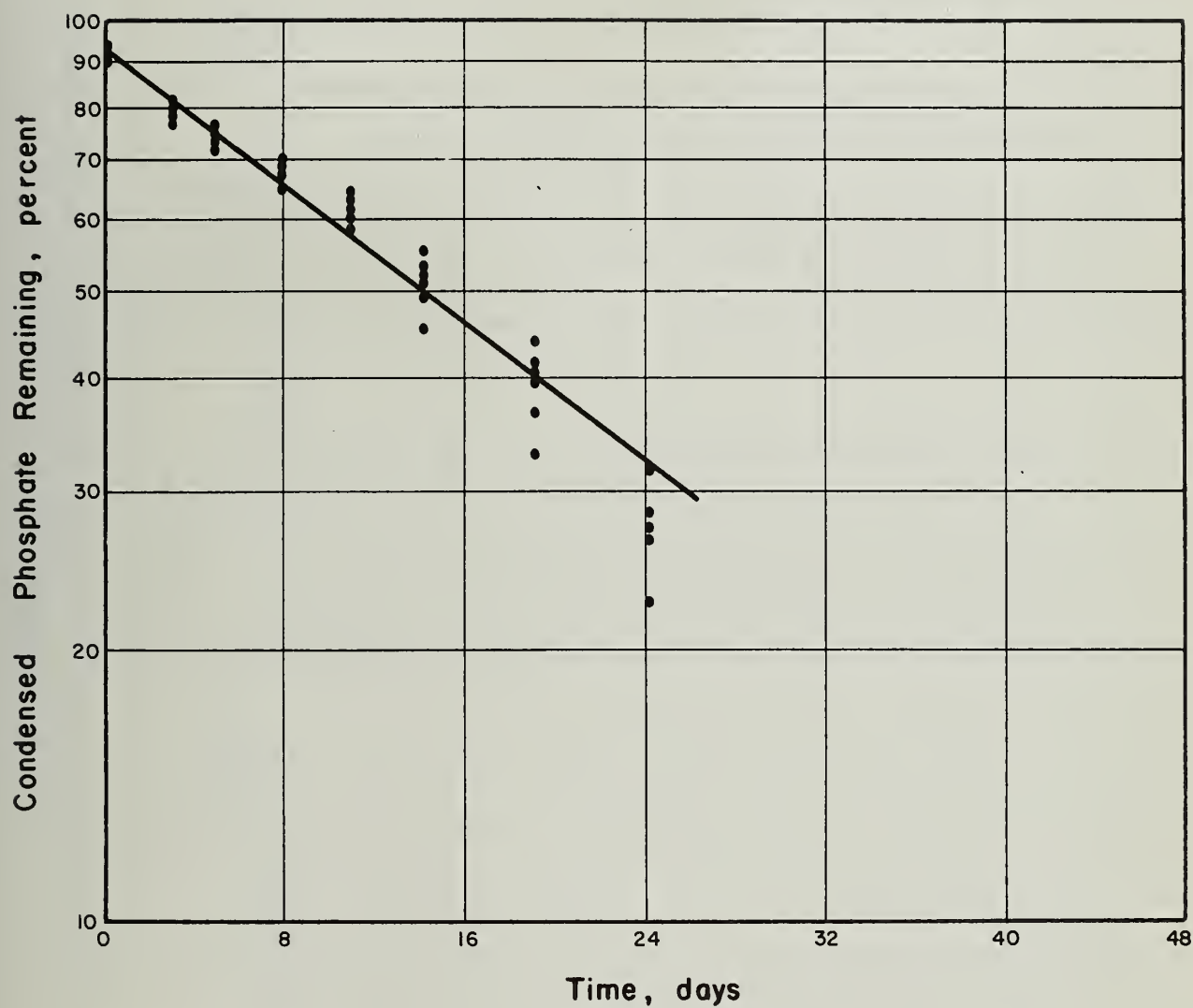


FIGURE 2. Degradation of 3.0 ppm (P_2O_5) TSPP in six portions of the same Ficklin A water sample.

TABLE 1

Chemical and Physical Characteristics of Natural Waters Used for Storage Studies

Storage Run No.	Source	Date Collected	Temp ^o F.	Dissolved Oxygen, ppm	Phosphorus, ppm P ₂ O ₅		Hardness, ppm CaCO ₃		Alkalinity, ppm CaCO ₃	pH	Turbidity ppm
					Ortho	Ortho + Hydrolyzable	Total	Calcium			
1	Mattoon	9/21/55	-	-	0.00	0.00	320	-	116	8.3	16
2	Bloomington	11/17/55	46	11	0.02	0.23	209	86	154	8.0	11
3	Kincaid	11/18/55	46	11	0.00	0.00	172	101	128	8.1	2
4	Springfield	11/18/55	51	11	0.00	0.00	170	100	120	8.0	15
5	Danville	12/6/55	35	13	0.09	0.11	330	180	210	8.0	6
6	Danville	2/21/56	-	-	0.11	0.20	223	128	129	8.0	33
7	New Athens	4/16/56	55	11	0.10	0.24	312	185	191	8.1	76
8	New Athens	4/30/56	61	7	0.15	0.34	290	185	180	7.7	98
9	New Athens	5/21/56	70	7	0.40	0.58	334	175	204	8.1	97
10	Bondville	9/29/56	58	12	0.82	0.96	310	169	298	8.1	0
11	Ficklin A	9/29/56	62	9	0.19	0.26	250	104	290	8.2	19
	Ficklin A	10/8/56	56	12	0.14	0.19	274	98	292	8.4	14
	Shelbyville	10/8/56	61	6	0.18	0.29	432	250	266	7.4	39

TABLE 1 CONT

Storage Run No.	Source	Date Collected	Temp F.	Dissolved Oxygen, ppm	Phosphorus, ppm P ₂ O ₅		Hardness, ppm CaCO ₃ Total	Alkalinity, ppm CaCO ₃	pH	Turbidity ppm
					Ortho	Ortho + Hydrolyzable				
12	Shelbyville	10/15/56	62	8	0.02	0.13	430	242	8.1	22
	Vandalia	10/15/56	70	9	0.22	0.42	354	192	8.1	98
	Bondville	10/29/56	46	9	0.04	0.09	334	59	7.4	48
	Ficklin A	10/29/56	52	10	0.17	0.21	218	55	7.9	32
	Ficklin B	10/29/56	53	5	0.13	0.98	740	602	6.6	90
13	Shelbyville	10/29/56	58	4	0.11	0.17	412	210	7.3	48
	Vandalia	10/29/56	60	9	0.17	0.25	322	131	7.8	24
	Carlyle	10/29/56	63	7	0.16	0.28	302	120	7.4	60
	New Athens	10/29/56	58	8	0.20	0.32	254	114	7.3	50
	Bondville	11/12/56	40	11	0.06	0.06	350	192	7.8	24
14	Ficklin A	11/12/56	45	12	0.16	0.20	222	102	8.6	22
	Ficklin B	11/12/56	47	10	0.38	0.69	1050	893	7.7	19
	Shelbyville	11/12/56	49	6	0.08	0.16	490	264	7.9	22
	Vandalia	11/12/56	53	12	0.14	0.19	342	174	8.2	21
	Bondville	12/3/56	-	12	0.13	0.15	-	-	8.2	12

Storage Run No.	Source	Date Collected	Temp °F.	Dissolved Oxygen, ppm	Phosphorus ppm P ₂ O ₅		Hardness ppm CaCO ₃	Alkalinity, ppm CaCO ₃	pH	Turbidity ppm
					Ortho	Ortho + Hydrolyzable	Total			
15	Ficklin A	12/3/56	-	12	0.35	0.40	246	116	8.4	9
	Ficklin B	12/3/56	-	10	0.19	0.34	890	764	7.7	9
	Shelbyville	12/3/56	-	10	0.92	0.92	712	525	8.0	7
	Vandalia	12/3/56	-	11	0.16	0.20	418	100	8.1	9

condition of storage, which can be identified by the following abbreviations:

Nonfiltered samples stored under quiescent conditions - NFQ

Nonfiltered samples stored under semi-quiescent conditions - NFSQ

Nonfiltered samples stored under turbulent conditions - NFT

Filtered samples stored under quiescent conditions - FQ

Filtered samples stored under semi-quiescent conditions - FSQ

Filtered samples stored under turbulent conditions - FT

The condensed phosphate compound used and the amount added and the method of filtration used in pretreating the FQ, FSQ, and FT samples is also indicated. Representative plots of results for two of the storage runs are shown in Figures 3 and 4.

From these data, it is apparent that the rate of degradation of STP varies in different surface waters. An attempt to explain this variation in rate, on the basis of the total hardness, calcium hardness and alkalinity in the raw water sample, proved unsuccessful. However, there was an indication that half life decreased with increasing amounts of hydrolyzable phosphate originally present in the water sample.

The chemical characteristics of the water samples were also determined at various intervals during the storage period. Although a change in total hardness and/or pH was noted in several of the stored samples, it was impossible to draw any conclusions from the results.

A very significant observation to be made concerning the results presented in Table 2 is the general difference in the rate of degradation between the filtered (FQ, FSQ, and FT) and nonfiltered (NFQ, NFSQ, and NFT) samples. With the exception of the two runs made with Danville water, filtered water consistently degraded the STP more slowly than the nonfiltered samples. In addition

TABLE 2

General Storage Studies of Various Illinois Surface Waters

Storage Run No. & Source	Storage [*] Condition	Phosphorus Cpd. Added	Amt. Cpd. Added as ppm P_2O_5	Half Life Days	Pretreatment Conditions
1 Mattoon	NFQ	STP	9.16	11.0	Filtered through paper & membrane filter
	NFSQ	"	"	14.5	
	NFT	"	"	19.5	
	FQ	"	"	31.5	
	FSQ	"	"	37.0	
	FT	"	"	45.0	
2 Bloomington	NFQ	STP	2.2	6.0	Filtered through cotton & paper
	NFSQ	"	"	7.0	
	NFT	"	"	8.0	
	FQ	"	"	27.0	
	FSQ	"	"	17.0	
	FT	"	"	34.0	
3 Kincaid	NFQ	STP	2.2	13.5	Filtered through cotton & paper
	NFSQ	"	"	13.9	
	NFT	"	"	15.0	
	FQ	"	"	24.6	
	FSQ	"	"	25.0	
	FT	"	"	26.0	
4 Springfield	NFQ	STP	2.2	28.5	Filtered through cotton, paper, and membrane filter
	NFSQ	"	"	26.0	
	NFT	"	"	29.9	
	FQ	"	"	33.5	
	FSQ	"	"	72.0	
	FT	"	"	36.0	

TABLE 2 CON'T

Storage Run No. & Source	Storage* Condition	Phosphorus Cpd. Added	Amt. Cpd. Added as ppm P_{2O_5}	Half Life Days	Pretreatment Conditions
5 Danville	NFQ	STP	2.2	4.2	Filtered through cotton, paper & membrane filter
	NFSQ	"	"	14.0	
	NFT	"	"	17.0	
	FQ	"	"	1.0	
	FSQ	"	"	1.9	
	FT	"	"	13.3	
6 Danville	NFQ	STP	2.2	6.5	Filtered through paper & membrane filter
	NFSQ	"	"	7.3	
	NFT	"	"	10.0	
	FQ	"	"	8.0	
	FSQ	"	"	14.0	
	FT	"	"	3.0	
7 New Athens	NFSQ	STP	2.2	2.4	
	NFT	"	"	3.0	
	NFSQ	TSPP	"	2.5	
	NFT	"	"	3.6	
8 New Athens	NFSQ	STP	2.2	2.2	
	NFT	"	"	2.1	
	NFSQ	TSPP	5.5	7.5	
	NFT	"	"	5.4	
9 New Athens	NFSQ	STP	2.2	0.4	
	NFT	"	"	0.6	
	NFSQ	TSPP	2.2	1.0	
	NFT	"	"	0.5	

*NFQ - Nonfiltered Quiescent

NFSQ - Nonfiltered Semi-Quiescent

NFT - Nonfiltered Turbulent

FQ - Filtered Quiescent

FSQ - Filtered Semi-Quiescent

FT - Filtered Turbulent

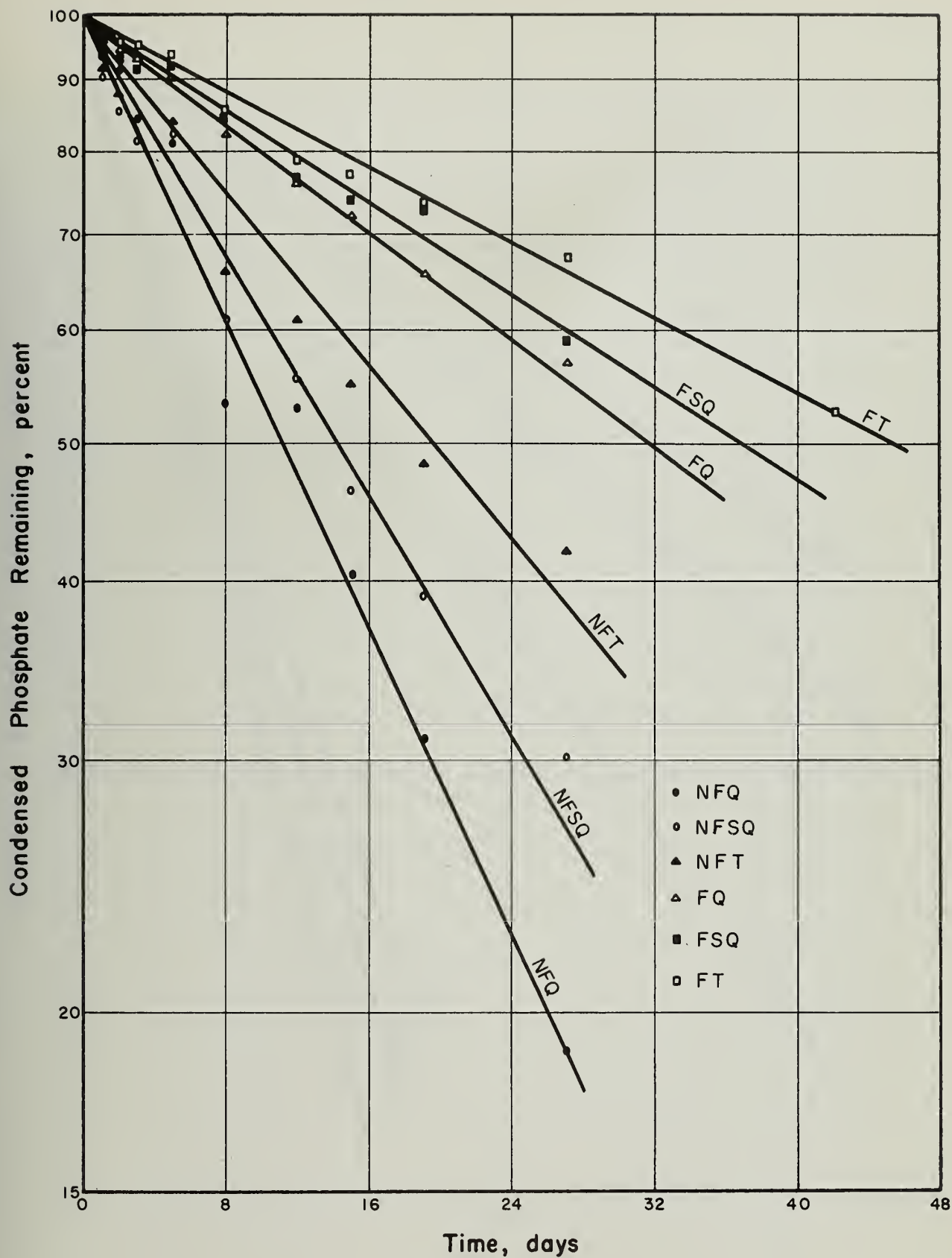


FIGURE 3. Degradation of 9.16 ppm (P_2O_5) STP in Mattoon water.

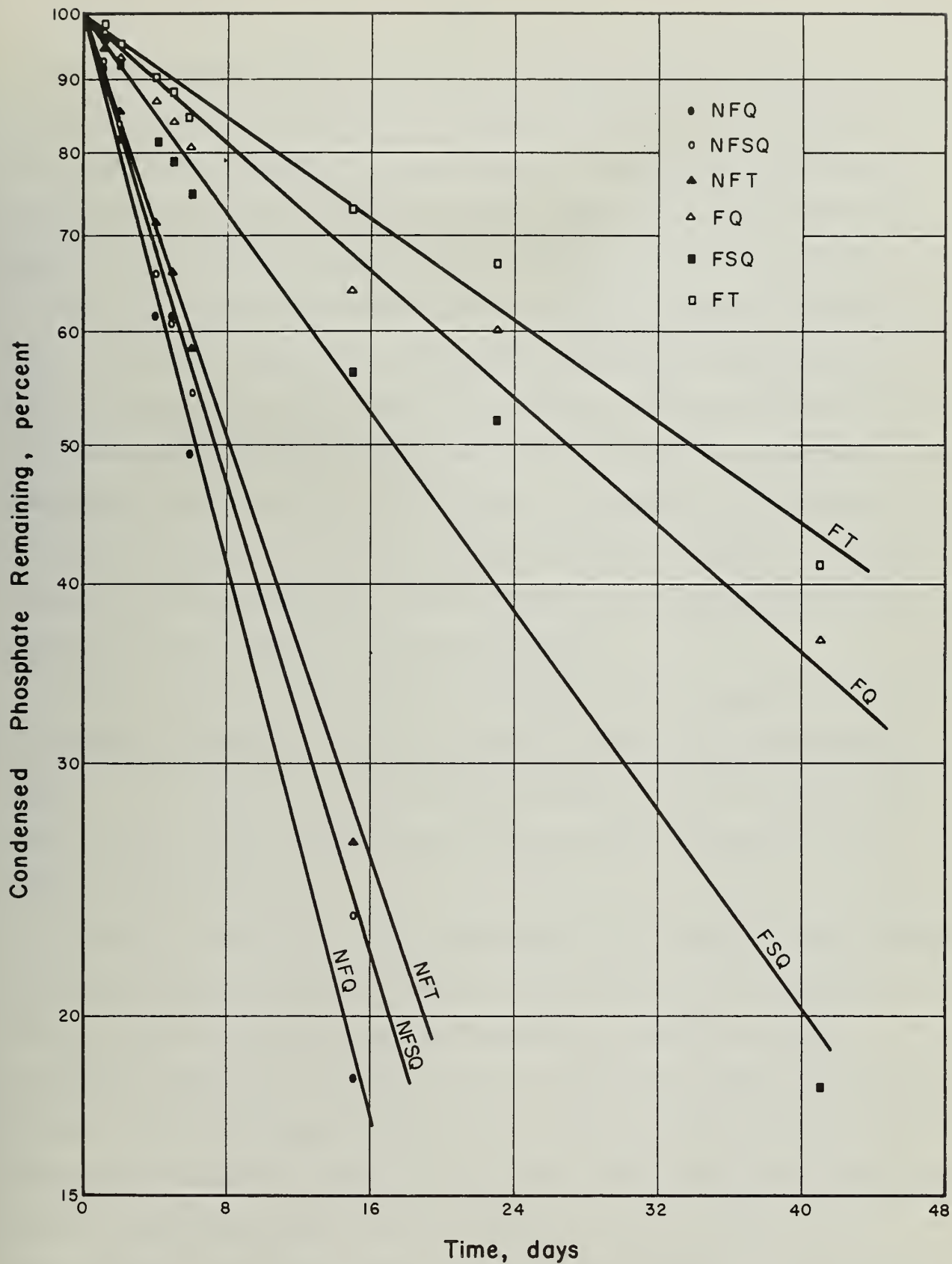


FIGURE 4. Degradation of 2.2 ppm (P_2O_5) STP in Bloomington water.

to removing suspended solids, the filtering methods employed reduced the bacterial population in the water. This was confirmed by bacterial plate counts made before and after filtration and by a comparison of counts made on both the filtered and nonfiltered samples. These observations definitely indicate that biological life accelerates the rate of degradation of STP.

The results of the two Danville studies were quite unusual. In each study, there was at least one filtered sample which showed a much shorter half life than all the other samples. Furthermore, the overall results in both studies were definitely in contrast to those found with the Mattoon, Bloomington, Kincaid and Springfield studies. A comparison of the chemical and physical characteristics of the raw waters, change in composition during storage, and the bacteriological results failed to give any explanation for the unusual results found with the Danville waters.

Table 2 also shows that the rate of degradation was, in general, less in the turbulent samples than in the corresponding quiescent and semi-quiescent samples. In considering all of the available data, including the results of the dissolved oxygen measurements made during storage, no reason for this condition has been found.

In order to compare the rate of degradation of STP and TSPP, three separate studies were made using New Athens water. These results are also shown in Table 2. Considering each storage run separately, a comparison of the corresponding NFSQ and NFT samples containing added STP and TSPP, respectively, indicates that TSPP degrades more slowly than STP in all but one case, the NFT samples of Run Number 9. Caution should be exercised in evaluating these data, especially that of Run Number 7 and 9, since the half life values are all relatively short. The larger magnitude of difference between the STP and TSPP samples of Run Number 8 is probably due to the combined effect of different

compounds and concentrations.

In an attempt to evaluate the effect of biological life and inert suspended matter on the rate of degradation of STP, various pretreatment methods were employed using Mattoon water. The membrane filter techniques was used to remove inert suspended matter having a particle size greater than 0.5 micron, and to reduce the initial biological population. Autoclaving was also used, and did produce sterile conditions in the sample. However, analysis of the raw water before the addition of STP showed that autoclaving altered its chemical characteristics. The following changes were found:

	<u>Raw Water</u>	<u>Autoclaved Raw Water</u>
pH	8.4	8.1
Total Hardness	257 ppm	202 ppm
Calcium Hardness	151 ppm	101 ppm
Alkalinity	136 ppm	83 ppm

This difference in chemical composition negates the complete acceptance of the results of this study. However, several interesting observations can be made from the data given in Figure 5. The control sample, which was not pretreated, shows a half life value of 4 days; while that of the membrane filtered sample (MF) is 9.7 days. The other two samples, autoclaved (Auto.) and membrane filtered plus autoclaved (MF & Auto.), show a very slow rate of degradation of STP.

Bacterial counts showed that all three of the pretreated samples were sterile at the beginning of the experiment before the addition of STP. Subsequent examinations indicated that bacterial contamination occurred when the bottles were opened for sampling. The MF sample became contaminated immediately, while the other two showed growth on the 8th day following initiation of the study.

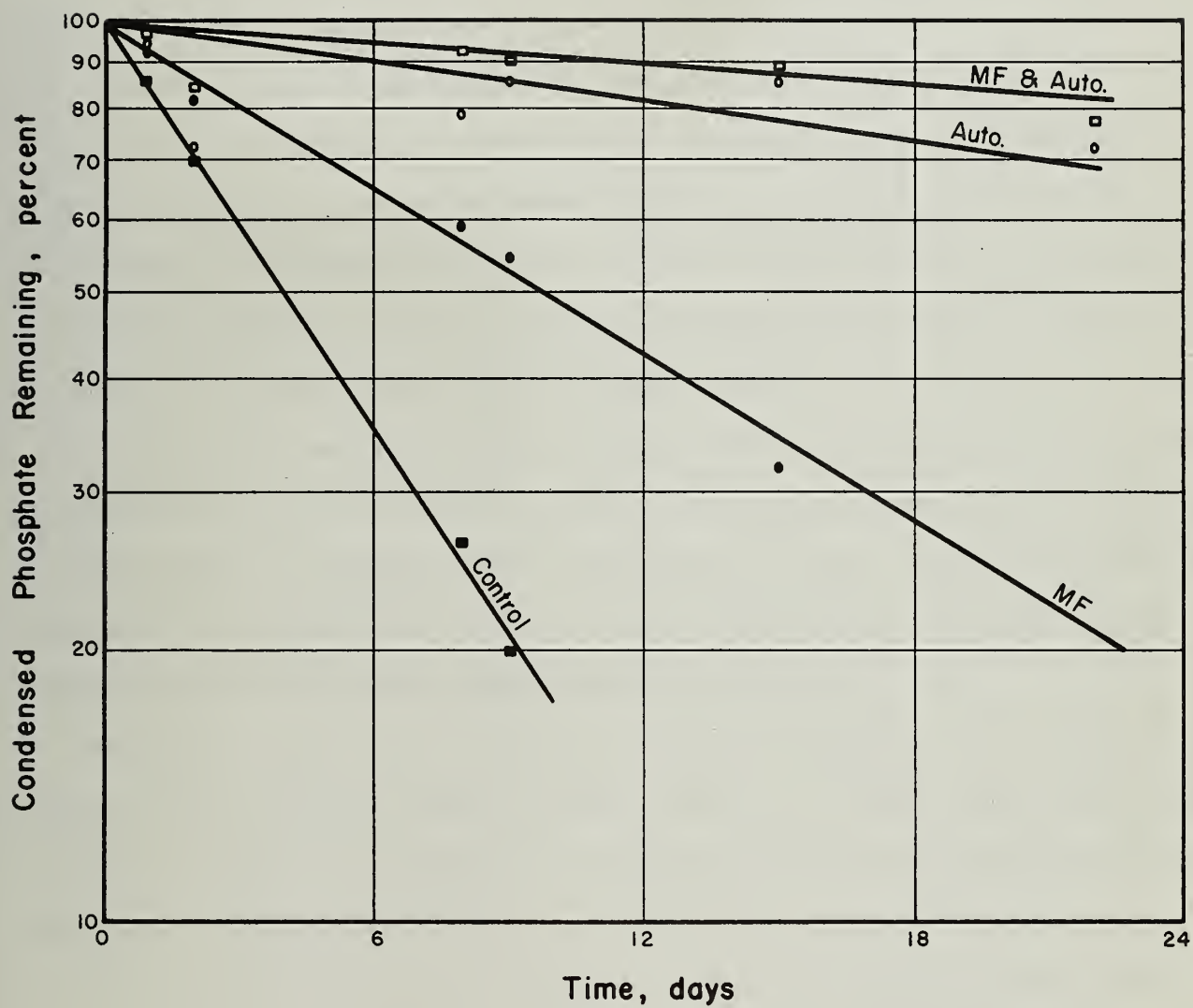


FIGURE 5. Degradation of 2.2 ppm (P_2O_5) STP in Mattoon water using various pretreatment methods.

Considering all of the factors associated with this study, there was still a very definite indication that the rate of STP degradation was affected by suspended matter and biological life.

Table 3 gives the results of the more extensive storage studies made using waters collected at various locations along the Kaskaskia River. In these studies, STP was added to all of the samples in order to give a concentration of 3.0 ppm (P_2O_5), and all samples were stored under nonfiltered, turbulent conditions. From these results, it is quite evident that there is considerable variation in half values for the waters collected at different locations on any given date. It is also quite apparent that the rate of degradation of STP varies in samples collected at the same location but at different times.

In initiating several of these studies, bacterial plate counts were made on the raw waters before the addition of STP. The results showed that the Ficklin B sample generally gave the highest total bacterial count. This quite probably accounts for the consistently greater rate of degradation in this sample when compared to the other samples collected at any one time.

Because of organic pollution above the Ficklin B station, C.O.D. measurements were made on the raw water samples used in Run No. 13. These results are given in Table 4. Except for the Shelbyville sample, there is an indicated correlation between half life and C.O.D.

A comparison of the rate of degradation of 3.0 ppm (P_2O_5) of STP and TSPP in individual portions of a Ficklin A water sample, under nonfiltered turbulent conditions, is shown in Figure 6. Six (6) separate portions of water, three (3) containing STP and three with TSPP, were stored. The mean half life value for the STP samples was 25 days while that of the TSPP samples was 38 days. Therefore, these values and the data presented in Figure 6 show that TSPP has greater stability, or a slower rate of degradation, than STP. These results agree

TABLE 3

Half Life Values for the Kaskaskia River Storage Studies
 Using STP at a Concentration of 3.0 ppm (P_2O_5)
 Under Nonfiltered Turbulent Condition

Coll. Date & Run No. Location	9/29/56 10	10/8/56 11	10/15/56 12	10/29/56 13	11/12/56 14	12/3/56 15
Bondville	13.3			10.0	27.5	32.0
Ficklin A	3.0	11.0		14.0	18.5	26.0
Ficklin B				0.4	0.8	1.0
Shelbyville		7.4	8.0	9.0	8.5	24.0
Vandalia			3.1	5.5	9.5	6.0
Carlyle				8.0		
New Athens				8.0		

TABLE 4

Half Life and C.O.D. Values for Kaskaskia River Samples
Collected October 29, 1956 (Table 3, Run No. 13)

Location	Half Life, Days	C.O.D., ppm
Ficklin B	0.4	87.6
Shelbyville	9.0	55.8
Vandalia	5.5	31.9
New Athens	8.0	31.9
Carlyle	8.0	23.9
Bondville	10.0	23.9
Ficklin A	14.0	12.0

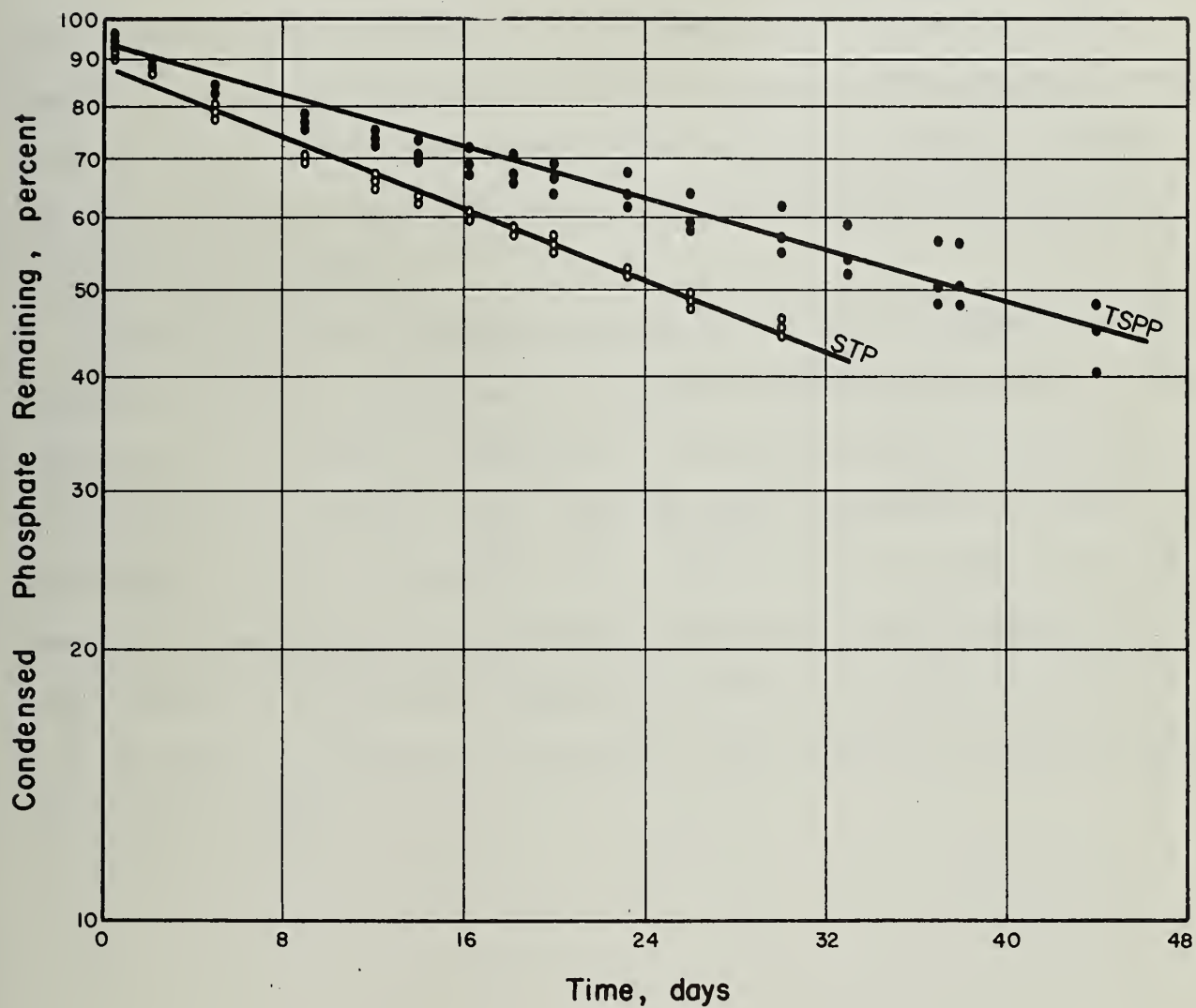


FIGURE 6. Degradation of three portions each of STP and TSPP in the same Ficklin A water sample - 3.0 ppm (P_2O_5).

with the observations made using New Athens waters and reported in Table 2, but are in contrast to the data shown in Figures 1 and 2. Although these later two figures represent data on the same source of water, Ficklin A, the difference in results presented in Figures 1 and 2, taken together and compared with Figure 6, can be accounted for by considering the fact that the water samples in these three storage studies were collected on different dates. Therefore, it can be concluded that, when the same natural water sample, considering both source and time of collection, is used for storage, STP degrades at a greater rate than TSPP.

A very limited study was made using non-sterile distilled water in order to evaluate the effect of temperature and condensed phosphate concentration. With respect to the influence of temperature, it was observed that by increasing the temperature of storage by 13°F . that the rate of degradation increased approximately 5 fold. In another study, 2.75 and 9.16 ppm as P_{2}O_{5} of STP was added to two samples of distilled water, respectively, and the samples stored under quiescent conditions at a temperature of 83°F . The half life of the 2.75 ppm sample was found to be 0.6 day while that containing the larger amount of STP was 6.3 days.

IV. DISCUSSION AND CONCLUSIONS

There have been a number of operational and research reports to the effect that synthetic detergents, which include condensed phosphates, interfere with the coagulation and sedimentation processes in the treatment of water supplies (8) (12) (13) (14). Because of the inherent peptizing and dispersing properties of condensed phosphates, it is logical to suspect that these compounds could interfere with these processes. Knowing that these condensed phosphates could pass through sewage treatment plants into receiving streams, their persistence or degradation in natural waters becomes important. This might be particularly important where a community uses a raw water supply which upstream receives an effluent from a sewage treatment plant. Therefore, the objective of this phase of the investigation was to determine whether condensed phosphates underwent hydrolytic degradation in natural water to form orthophosphate and, if they did, to study the conditions which affect this reversion.

It has been definitely established that degradation of condensed phosphates, as represented by STP and TSPP, does occur in natural waters. This has been shown in this study, and in the study by Smith, Cohen and Walton (8), whose report appeared since the initiation of this investigation.

Where experimental conditions were essentially the same, it was quite apparent that natural waters, collected at different locations, degraded the condensed phosphates, STP and TSPP, at different rates. Green (6) has reported that calcium increased the rate of degradation. In this study, even though both the greatest rate and concentration of calcium generally were observed in the Ficklin B sample, there did not appear to be a direct relationship. Actually, although the chemical and physical composition of the natural waters differed, there was no distinct correlation between rate of degradation and these various characteristics. Considering the inorganic chemical characteristics determined, the only possible exception was with the hydrolyzable phosphate concentration

originally present. Natural raw waters which had a considerable amount of hydrolyzable phosphate present generally gave the shortest half life when condensed phosphate was added. Furthermore, there was an indication that half life decreased as the hydrolyzable phosphate concentration present in the natural raw water increased. Because it was found that the analytical procedure for condensed phosphate employed in this study also detected certain organic phosphates, it is difficult to explain the possible significance of this observation. If an explanation does exist, it might well be related to the biological aspect associated with the degradation of condensed phosphate.

Except for the studies made with Danville water, it was quite apparent that filtration decreased the rate of degradation. It was found that all of the filtration methods employed reduced the concentration of suspended solids, including various forms of biological life, originally present in the natural waters. Furthermore, it has been shown that the membrane filter technique effectively removes all organisms, producing a sterile filtrate. This is related to the fact that the membranes as fabricated today have a calculated pore size of 0.4 to 0.45 micron. Therefore, all particles, including bacteria, larger than 0.5 microns were quantitatively retained on the membrane. Although numerous attempts were made, using sterile equipment and aseptic precautions, to obtain sterile samples for storage, contamination generally occurred during the filtering operation. This can be explained by the fact that the large amount of water required necessitated that a number of membranes be used and this meant a great deal of manipulation. It was also possible for the sample to become contaminated during the opening of the storage bottle for the purpose of obtaining samples for analysis. However, bacterial plate counts confirmed the fact that the bacterial population was significantly reduced by the filtration methods employed.

To further evaluate the biological effect, a study was made in which two samples of Mattoon water were autoclaved. One of these samples was subjected to membrane filtration before autoclaving in order to also remove the inert suspended matter. In addition to these two samples, there was a membrane filtered sample and an untreated control. Because autoclaving was found to change the chemical composition of the raw water, the results of this study cannot be considered to be conclusive. However, the greatest rate of degradation of 2.2 ppm (P_2O_5) of STP was found in the untreated control, while stability progressively increased in the membrane-filtered, autoclaved, and membrane-filtered-plus-autoclaved samples, respectively. Bacterial plate counts indicated that all three of the pretreated samples were initially sterile, but that subsequent contamination occurred. From this study, it appeared that both suspended matter and biological life affected the rate of STP degradation.

A series of studies, using waters collected at various sampling stations along the Kaskaskia River, showed that the rate of degradation of STP varied in the different samples even though they were all obtained on the same date. It was also found that the stability of STP differed in waters collected at the same station, but at different times. The greatest rate of degradation of STP was observed in the Ficklin B sample regardless of time of collection. It was significant to note that bacterial plate counts of a number of the raw water samples used in this series of experiments consistently showed that the water from this station had the highest count.

Considering this same series of studies, C.O.D. measurements were made on all the raw water samples collected at the different stations on one particular day. Of the eight samples collected and stored, there was only one exception

to the observation that the rate of degradation of STP increased as the amount of C.O.D. in the raw water increased. Thus, there was an indicated correlation between organic matter in the raw water and half life. Furthermore, the greatest amount of C.O.D. was found in the Ficklin B sample. This fact could well be related to the greater amount of biological life observed in this source of water, which in turn might account for the accelerated rate of degradation of STP.

In summary, it appeared that biological life, through enzymatic activity, definitely influences the degradation of condensed phosphate and the rate at which it occurs. This observation is in agreement with the conclusions reported by Summer and Myrback (9) and Karl-Kroupa, et al. (3).

It was found that STP degraded at a more rapid rate than TSPP when the same sample of natural water was used. If two water samples from the same source, but collected at different times, were used to determine the rate of degradation, it was possible to observe that TSPP degraded faster in one sample than did STP in the other. This indicated that the chemical, physical and/or biological properties of natural water can influence the degradation of condensed phosphate. Since these properties are subject to change in natural waters, only when the same sample is used can the rate of STP and TSPP be compared. Smith, et al. (8) also found that STP generally degraded faster than TSPP. However, this observation was made on separate samples of Ohio River Water and, therefore, cannot be directly compared. Working with domestic sewage, Sawyer (7) found that STP degraded much more slowly than TSPP. This was definitely in contrast to the findings in this study.

Using non-sterile distilled water to evaluate the effect of temperature and concentration of condensed phosphate on degradation, it was shown that an increase in temperature increased the rate of degradation while an increase in

concentration appeared to decrease the rate. A 13°F. rise in temperature was found to increase the rate approximately five fold. The data also showed that with a STP concentration of 2.75 ppm (P_2O_5) that the half life was 0.6 days or that 1.38 ppm was degraded in that length of time. Another sample of distilled water, to which 9.16 ppm (P_2O_5) of STP was added, gave a half life value of 6.3 days. Thus, 4.58 ppm was hydrolyzed in 6.3 days. Therefore, it was calculated that the sample with the smaller amount of STP degraded the condensed phosphate at ten times the rate indicated by the sample with the larger concentration of STP. However, the experimental conditions in this single study were such that this relationship should be studied further before any definite conclusion is drawn.

V. SUMMARY

The results of these laboratory studies on the degradation of condensed phosphates in natural waters, using sodium tripolyphosphate (STP) and tetrasodium pyrophosphate (TSPP), indicated the following:

1. Condensed phosphates, as represented by STP and TSPP, were subject to hydrolytic degradation in natural waters.
2. The rate of degradation varied in different natural waters, having different chemical and physical characteristics. With the possible exception of the concentration of organic matter and hydrolyzable phosphate in the natural raw water, both of which appeared to increase the rate of degradation, there seemed to be no correlation between rate and these characteristics.
3. Natural waters, collected at the same time but at different locations along a single river, gave different rates of degradation. Similarly, the rate of degradation varied in natural waters, collected at different times but at the same location.
4. Filtration of the raw water definitely decreased the rate of degradation. This result, along with bacteriological data and additional observations, indicated that biological life exerted an effect on the rate of degradation.
5. Of the condensed phosphates studied, STP degraded more rapidly than TSPP when the same natural water was used for study. However, if the degradation of STP and TSPP was studied separately, using either different natural waters or different samples of the same water, TSPP could be observed to degrade faster than STP.

6. Using distilled water, the rate of degradation increased with temperature, but appeared to decrease as the concentration of condensed phosphate was increased.

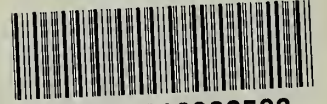
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